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Keywords
Lanthanide additives, Cu-YSZ, Cermet anodes, Molybdena, Fuel cells, Direct oxidation

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An Examination of Lanthanide Additives on the Performance of Cu-YSZ Cermet Anodes

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Abstract

The effect of various lanthanide additives on the performance of Cu-YSZ (yttria-stabilized zirconia), cermet anodes for solid-oxide fuel cells (SOFCs) was investigated at 973 K for H_2 and the direct oxidation of butane. In all cases, the lanthanide oxides were added to the SOFC by impregnation of a porous YSZ matrix with aqueous solutions of the nitrate salts, followed by decomposition of nitrate ions by calcination. Ceria was found to be significantly more effective in promoting SOFC performance compared to the other lanthanides, and the performance of the lanthanide additives followed the catalytic activity observed for butane oxidation with 100 torr each of butane and O_2. Samaria doping of ceria led to a slight decrease in performance but also decreased the catalytic active of ceria for butane oxidation. Membrane-reactor studies with propylene fed to Cu-molybdena-YSZ anodes at 723 K showed a high selectivity to acrolein, although Cu-ceria-YSZ anodes showed only total oxidation products under these conditions, implying that the catalytic properties of the oxides must be important. Finally, the application of these results to improved SOFC for direct oxidation of hydrocarbons is discussed.

Introduction

Fuel cells that operate by direct oxidation of hydrocarbons could have significant advantages over conventional fuel cells that require hydrogen as the fuel. First, most hydrogen is prepared by steam reforming of methane. Unless steam reforming is carried out *in situ*, this process leads to a decreased efficiency for the system. Second, unlike hydrocarbon fuels, hydrogen is not readily available and an entire infrastructure will need to be built in order to use it on wide scale. Third, significant problems associated with hydrogen storage have yet to be solved. For all of these reasons, it would be highly desirable to operate fuel cells on the readily available fuels that are currently used in other applications.

Direct oxidation of hydrocarbons is theoretically possible in a solid-oxide fuel cell (SOFC); and we have recently demonstrated that SOFC with Cu-based anodes are able to directly convert a wide range of hydrocarbon fuels, including synthetic diesel fuel, to electrical energy [1-4]. Briefly, SOFC generates electricity through the reduction of O_2 to O^{2-} anions at the cathode, transfer of the anions through an electrolyte that is an electronic insulator (usually yttria-stabilized zirconia, YSZ), and finally the oxidation of the fuel by O^{2-} anions at the anode. Because the anode must be an electronic conductor and have a good thermal-expansion match with the electrolyte, it is usually composed of a ceramic-metal (cermet) composite, in which YSZ is the ceramic component. Although Ni is the common choice for the metal in the anode cermet [5], it cannot be used for direct-oxidation fuel cells because it catalyzes formation of carbon deposits [6]. Carbon formation can be avoided if the anode cermet is based on catalytically inert metals, and Cu is known to be a poor catalyst for C-C bond breaking and formation.

Because Cu is a relatively poor oxidation catalyst, another component must be added to the anode cermet for hydrocarbon oxidation. In past work, we have shown that the addition of ceria to a Cu-YSZ cermet significantly enhances the performance of the cell, especially for hydrocarbon fuels [1,3]. We have suggested that the ceria plays a catalytic role in composite anode, since ceria is an excellent oxidation catalyst, widely used in this role in automotive three-way catalysis [7]. Unlike transition metals, ceria does not promote C-C bond formation and, therefore, does not tend to form carbon deposits.

In this paper, we will discuss experiments designed to better understand the role of ceria in direct-oxidation, SOFC and to determine whether other oxides could be used in place of ceria. The results demonstrate that, although the presence of ceria may play multiple roles in the

anodes of these fuel cells, ceria must also be providing catalytic activity for hydrocarbon oxidation.

Experimental

The methods we have used for preparing Cu-based cermets have been discussed in other papers [3]. Because oxides of Cu melt at temperatures lower than that required for sintering of the oxide components, the preparation procedures involved preparing a porous matrix of YSZ, impregnating this porous matrix with Cu salts, and finally reducing the salts to metallic Cu. An additional advantage to this method is that any oxide catalyst can also be added to porous matrix in the same manner as the Cu salts, even if these oxides tend to form solutions with YSZ at higher temperatures.

In the first step, the dense electrolyte layer and the porous YSZ matrix were prepared simultaneously by tape-casting methods. A two-layer, green tape of YSZ (yttria-stabilized zirconia, Tosoh, 8 mol% Y_2O_3) was made by casting a tape with graphite and poly-methyl methacrylate (PMMA) pore formers over a green tape without pore formers [3]. Firing the two-layer tape to 1800 K resulted in a YSZ wafer having a dense side, 60 μm thick, supported by a porous layer, 400 μm thick. Water porosimetry showed the porosity of the porous layer was ~68%. Next, a 50:50 mixture of YSZ and LSM ($La_{0.8}Sr_{0.2}MnO_3$, Praxair Surface Technologies) powders was applied as a paste onto the dense side of the wafer, then calcined to 1400 K to form the cathode. Third, the porous YSZ layer was impregnated with an aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ or other oxide precursor and calcined to 723 K to decompose the nitrate ions and form CeO_2 or other oxide. After addition of the oxide, the porous layer was impregnated with an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ and again heated to 723 K in air to decompose the nitrates. The anodes in all of these studies were 10 wt% oxide and 20 wt% Cu, with the exception of the Cu-only cell, which contained 20 wt% Cu, but did not contain any oxide except YSZ.

Electronic contacts were formed using Pt mesh and Pt paste at the cathode and Au mesh and Au paste at the anode. The cells, having a cathode surface area of 0.45cm^2, were sealed onto 1.0-cm alumina tubes using Au paste and a zirconia-based adhesive (Aremco, Ultra-Temp 516). The entire cell was then placed inside a furnace and heated to 973K at 1.25 K/min in flowing H_2, using the same experimental apparatus for both the fuel-cell and membrane-reactor measurements, as shown in Fig. 1. Measurement of the cell potential as a function of current was used as the primary means for determining the cell performance. Since the cathodes and

electrolytes were essentially identical in all cases, the relative fuel-cell performances provide a good measure of anode performance. Although we did not perform any long-time stability tests, all of the cells we examined showed stable performance in H_2 and butane over a period of at least several hours.

As shown in Fig. 1, the composition of the gases leaving the anode could be monitored by an on-line gas chromatograph, allowing the cell to be operated as a membrane reactor. For these studies, the cell potential was set by means of an external power supply, allowing significant currents to be achieved at lower operating temperatures where selective oxidation chemistry is to be expected [8]. The applied potential was kept below 1.5 V in order to avoid degradation of the YSZ structure. The membrane-reactor studies were carried out with pure propylene as the feed to the anode because partial oxidation of propylene to acrolein is known to occur on molybdena [8]. The gas chromatograph (Gow Mac, Series 580) was fitted with a 0.5-ml sample loop, and the rates of formation for acrolein and carbon dioxide were measured using Tenax GC 60/80 and Hayesep DIP 100/120 columns.

The catalytic properties of the oxides were examined using a quartz flow reactor with a quadrupole mass spectrometer (Leybold Inficon) as the detector. The catalyst powders were prepared by heating the nitrate salts to 723 K in air and grinding the resulting powder with a mortar and pestle. The surface areas of ceria and ceria-zirconia powders formed in this way were found to be between 30 and 35 m^2/g and the properties of the other oxides are believed to be similar [9]. The reactor was then loaded with 0.10 g of the metal-oxide powder and heated at a rate of 10 K/min. Butane-oxidation, light-off curves were measured at a total pressure of 1 atm, with partial pressures of 100 torr butane, 100 torr O_2, and the balance He. The reactor effluent was sampled at 15-second intervals by the mass spectrometer. After reaching the final temperature of 850 K, the sample was cooled at 10 K/min while monitoring the products to check whether hysteresis was important. In all cases, hysteresis was negligible and the conversions were the same whether the samples were being heated or cooled. Although the reaction conditions (excess hydrocarbon) were chosen to simulate the highly reducing conditions of the anode in the fuel cell, the ceria powder was a light yellow when it was removed from the reactor, indicating that ceria was primarily in its +4 oxidation state. Finally, the conversion of the empty tube was found to be insignificant, implying that the reaction was catalyzed by the oxides in each case.

Results

In past studies, we had observed that fuel cells made with Cu-YSZ anodes exhibited a much lower performance than cells with a Cu-ceria-YSZ anode [3]. In Figs. 2a and 2b, performance curves are shown for cells with Cu-YSZ (20 wt% Cu) and Cu-ceria-YSZ (20 wt% Cu, 10 wt% ceria) anodes at 973 K for 100% H_2 and 100% butane feed. For the Cu-ceria-YSZ cell, the open-circuit voltage (OCV) was 1.1 V for H_2, in good agreement with the value predicted by the Nernst Equation. The OCV for butane, 1.03 V, was slightly lower than the value of E_o, 1.12 V. The performance curves and maximum power density for butane were also slightly lower than for H_2, showing a maximum power density for butane of 0.13 W/cm^2, compared to 0.19W/cm^2 for H_2. As discussed elsewhere, the poorer performance for butane compared to H_2 probably results from catalytic limitations [3]. By comparison, the performance of the Cu-YSZ cell was poor. The OCVs were 1.12V and 1.04 V for H_2 and butane respectively, however, the maximum power densities were approximately 15% of the values obtained on the Cu-ceria-YSZ cell, being only 0.04 and 0.02 W/cm^2, respectively, for H_2 and butane.

To examine the role of ceria more closely, we measured the products formed by membrane reactors using Cu-ceria-YSZ and Cu-molybdena-YSZ anodes, both having 20 wt% Cu and 10 wt% added oxide. The equipment used was identical to that used in the fuel-cell measurements, except for the power supply used to fix the potential across the cells and the gas chromatograph for product analysis. Pure propylene was fed to the cells at a flow rate of approximately 0.3 cm^3/sec and a temperature of 723 K. Results for the Cu-ceria-YSZ anode are shown in Fig. 3a. No conversion of propylene was observed at open circuit and the conversion increased almost linearly with the applied current density. The points shown in the figure are the rates of CO_2 production calculated from the chromatographic analysis, while the line is the predicted CO_2 production rate based on Faraday's equation:

$$CH_2{=}CHCH_3 + 9O^{2-} \rightarrow 3CO_2 + 3H_2O + 18e^- \qquad \text{Equation 1)}$$

Since only traces of CO were observed and CO_2 and water were the primary products, the deviation between the line and the points represent a failure to close the mass balance, probably due to an uncertainty in the measured area of the GC calibration or flow-rate measurements.

Results for the Cu-molybdena-YSZ cell, shown in Fig. 3b, were different. Unlike ceria, which is a nonselective oxidation catalyst, molybdena is a selective catalyst for the partial

oxidation of propylene to acrolein (CH_2=CHCHO) and is used commercially for this process [8]. The primary product at low conversion was acrolein, produced according to the reaction:

$$CH_2=CHCH_3 + 2O^{2-} \rightarrow CH_2=CHCHO + H_2O + 4e^- \quad \text{Equation 2)}$$

Again, points on the curve were the measured rates of acrolein production and the line is the predicted production rate based on the current and the stoichiometry in Equation 2). At higher conversions, we observed significant amounts of CO_2 and water, sufficient to explain the difference between the measured rate of acrolein production and the current. It should be noted that others have also reported the electrochemical production of acrolein in a membrane reactor with molybdena in the anode [10-12].

We suggest that the results in Fig. 3 can be understood by the schematic of the three-phase-boundary (TPB) region of the anode shown in Fig. 4. Here, the oxide, either ceria or molybdena in our case, is oxidized by contact with the YSZ electrolyte. The propylene "fuel" reduces the oxide layer, forming primarily CO_2 and water in the case of ceria and acrolein in the case of molybdena. Finally, the ceria and molybdena catalysts are re-oxidized by oxygen atoms diffusing through the electrolyte. The primary role of Cu in this scheme is simply to remove electrons. This picture implies that the oxide catalyst must be in direct contact with the electrolyte for it to be effective. In agreement with this, we have observed that we obtain significantly better performance for fuel cells with Cu-ceria-YSZ anodes when the anodes are fabricated by first impregnating the porous YSZ matrix with ceria and then with Cu added in a later step [13]. Cells in which the Cu is added first, or in which the Cu and ceria are added simultaneously, show significantly lower power densities.

Based on the picture in Fig. 4, we decided to test whether other lanthanide oxides may also be effective catalysts and might lead to improved performance. Fig. 5 shows the light-off curves for butane oxidation with a number of lanthanide oxides, using experimental conditions described in the Experimental section. Ceria is the most active of these oxides and shows the lowest light-off temperature at 500 K. The light-off temperature for the next most active oxide, Eu_2O_3, was shifted upward by approximately 70 K. This represents a significant decrease in the catalytic activity, given that rates essentially always show an inverse Arrhenius, exponential temperature dependence. After Eu_2O_3, the activities decreased in the following order: Tb_4O_7, Pr_6O_{11}, Sm_2O_3, Yb_2O_3, ZrO_2, and La_2O_3. Others have reported a similar order for the activity of the lanthanide oxides for butane oxidation [14].

To determine the effectiveness of these oxides in a fuel cell, we prepared cells in the same manner as with the molybdena- and ceria-containing cells. Each oxide was impregnated into the YSZ matrix to a loading of 10 wt% oxide, then Cu was added to achieve a final loading of 20 wt% Cu. The OCV and general V-I characteristics for these cells were similar to that found for the cells with a Cu ceria-YSZ anode, but the power densities achieved were always significantly lower. This is shown in Fig. 6, which is a plot of the maximum power densities achieved with H_2 and butane on each of the oxides examined. The best performance was achieved with the addition of ceria into the anode. There also appears to be enhanced performance with Tb_4O_7, Eu_2O_3, and Yb_2O_3.

In addition to its catalytic properties, ceria is known to be an ionic conductor, a property which could be extremely important in the SOFC anode. Since samaria-doped ceria is known to have significantly better ionic conductivity than pure ceria, we also tested a cell in which a mixed solution of $Ce(NO_3)_3$ and $Sm(NO_3)_3$, in a ratio of 8:2, were co-impregnated into the porous YSZ to form the catalytic oxide. (A maximum in the ionic conductivity of doped cerias is known to occur at 20% Sm [15].) The V-I curves for this fuel cell at 973 K for H_2 and butane are shown in Fig. 7, together with the analogous results for pure ceria. While the results with the Sm-doped ceria are not dramatically different from that obtained with pure ceria, the performance is certainly not improved. Furthermore, a careful examination of data reported previously with ceria and with Sm-doped ceria also found a slightly lower performance with the doped ceria [2].

Since at least one report has suggested that Sm doping can lead to a decreased reducibility of ceria [16], we examined light-off curves for butane oxidation on a series of ceria powders doped with varying amounts of samaria. As in the fuel-cell case, the powders were prepared by drying of homogeneous, aqueous solutions of $Ce(NO_3)_3$ and $Sm(NO_3)_3$, after which the powders were heated to 723 K to form the oxides. The reaction results for this series of catalysts are shown in Fig. 8. Clearly, doping ceria with samaria decreases the activity of the powders dramatically. At a level of 20% Sm, the doped ceria shows an activity that is close to that of pure samaria. The fact that a fuel cell prepared with 20% Sm-doped ceria does show reasonable performance, even though the catalytic activity of this composition is low, suggests that the ionic conductivity may indeed be important, but that the decrease in catalytic properties counteracts any improvement achieved by doping with samaria.

Discussion

As demonstrated in earlier publications from our laboratory [1,3], the addition of ceria is crucial for obtaining reasonable performance in Cu-based cermets. At 973 K, we have observed an increase in the power densities by a factor of more than five upon the addition of ceria. The crucial question is this: What properties of ceria cause this large improvement in the performance? In this paper, we have argued that the oxide has an important role in catalyzing the hydrocarbon-oxidation reactions. Certainly, the membrane-reactor measurement in which ceria was replaced with molybdena strongly argue that catalysis is crucial. The selective oxidation of propylene to acrolein with the Cu-molybdena-YSZ anode can only be explained if molybdena is undergoing a redox reaction, presumably being oxidized by the electrolyte and reduced by the fuel. By inference, ceria is also likely acting as a catalyst. The fact that we achieved superior performance when ceria was added to the porous YSZ matrix prior to the addition of Cu also argues for the importance of having ceria in intimate contact with the YSZ electrolyte and for the importance of the catalytic properties. However, these results do not preclude the possibility that ceria may play other roles in the anode as well. Obviously, a complete understanding of how ceria enhances the anode performance could lead to even larger improvements if materials with even better properties could be used.

There clearly seems to be a correspondence between the catalytic activity for butane oxidation of the various lanthanide oxides and their effectiveness in promoting the anode performance. It is likely that butane oxidation is a good measure of the ease with which the various oxides can be reduced. Indeed, the fact that anode performance increased equally for H_2 and butane fuels would suggest that hydrocarbon-oxidation activities are not the crucial issue in this case. This contrasts with the results of Putna and coworkers, who observed that the addition of Rh to SDC anodes led to a significant improvement in the performance of fuel cells operating on methane, although the addition of Rh had essentially no effect on the performance of the cells with H_2 [17]. The results of Putna and coworkers are probably due to Rh having a larger promotional effect on the reduction of SDC by methane compared to reduction by H_2. Clearly, the addition of precious-metal catalysts to SOFC anodes deserves further investigation.

We are not the first to observe improved anode performance by the addition of lanthanides to the anode cermet. For example, Eguchi and coworkers reported that a Ni-ceria cermet exhibited better performance than a Ni-YSZ cermet [18]. They proposed that this was due to the ease with which ceria is reduced, essentially the same argument we have used in the above

discussion. However, Eguchi and coworkers also reported that the performance with Ni-praeseodymia cermets was even better than with Ni-ceria, although we found praeseodymia to be ineffective. This difference between our results and theirs may be due to the morphology of the cermet. Rather than having a bulk, ceria or praeseodymia phase, YSZ was the main oxide component in our samples.

Tsai and Barnett also reported significant improvements in the performance of Ni-YSZ cermet anodes when a 0.1-µm layer of yttria-doped ceria (YDC) placed between their YSZ electrolyte and a Ni-YSZ anode [19]. Because they also observed a lower anode resistance when they inserted a 0.1-µm layer of titania-doped YSZ (YZT) between the electrolyte and cermet anode, they argued that the YDC and YZT layers improved performance due to better charge transfer, resulting from higher mixed conductivity, in the three-phase boundary. Although YDC may well have better redox properties than YSZ, it is unlikely that YZT would be a better redox catalyst than YSZ.

Obviously, the reason we compared results for a Cu-based anode having Sm-doped ceria (SDC) with one having un-doped ceria was to look for the effect of ionic conductivity. Under the conditions of our experiment, SDC has improved ionic and electronic conductivity compared to pure ceria [20]. Unfortunately, our catalytic tests of butane oxidation suggest that SDC is much less reducible than pure ceria, so that the ionic conductivity and redox properties cannot be varied independently. The fact that our tests showed the performance with SDC to be similar to that with pure ceria may indicate that both redox and charge-transfer properties are important. If this is the case, the improved ionic conductivity of SDC may have been offset by the SDC being more difficult to reduce.

The experiments in this paper have clearly demonstrated that the addition of oxide compounds to the Cu-YSZ cermet anode can have a profound influence on the performance of the final cells. Although many questions remain about how these oxides improve performance, we suggest that this remains a fruitful avenue for further research to improve SOFC anodes.

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Conclusions

Lanthanide additives to SOFC anodes can have a profound effect on the performance of SOFC. Ceria is superior to the other lanthanides and this seems to be related to the ease with which ceria can be reduced by H_2 and hydrocarbon fuels. Samaria doping of ceria does not appear to be effective for enhancing performance with our anode geometries, in which the lanthanides are added to a porous matrix of YSZ.

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Figure Captions

Fig. 1 A schematic of the equipment used in the fuel-cell and membrane-reactor measurements.

Fig. 2 The performance curves for SOFC with Cu-ceria-YSZ (squares) and Cu-YSZ (triangles) anodes for H_2 (filled symbols) and butane (open symbols) at 973 K: a) V-I curves; b) the calculated power-density curves.

Fig. 3 Propylene conversion and product-selectivity results for the membrane-reactor measurements performed at 723 K with pure propylene as the feed. The results in a) were for the SOFC with a Cu-ceria-YSZ anode and the results in b) were for the Cu-molybdena-YSZ anode. In a), the points are the rate of CO_2 production and the line was calculated from the current density and Equation 1). In b), the points show the production of acrolein and the line was calculated from Equation 2).

Fig. 4 Schematic picture of the anode, three-phase boundary.

Fig. 5 Light-off curves for butane oxidation in 100 torr of butane and 100 torr of O_2. The results are for CeO_2 (■), Eu_2O_3 (△), Tb_4O_7 (●), Pr_6O_{11} (□), Sm_2O_3 (▲), Yb_2O_3 (○), ZrO_2 (◆), and La_2O_3 (◇).

Fig. 6 Maximum power densities achieved at 973 K for SOFC with Cu-RE-YSZ anodes, where RE is given on the ordinate. ■ show data for H_2 and ◆ show data for butane fuels.

Fig. 7 Performance curves for SOFC with Cu-ceria-YSZ (squares) and Cu-SDC-YSZ (triangles) anodes for H_2 (filled symbols) and butane (open symbols) at 973 K: a) V-I curves; b) the calculated power-density curves.

Fig. 8 Light-off curves for butane oxidation in 100 torr of butane and 100 torr of O_2. The results are for various levels of Sm doping in ceria: 0% Sm (◆), 5% Sm (◇), 10% Sm (■), 15% Sm (□), 20% Sm (▲), 100% Sm (△).